should lead to continued development of membrane systems for bioseparations.

See also: **II / Membrane Separations:** Microfiltration; Ultrafiltration.

Further Reading

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Membrane Preparation

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Background

A membrane (Latin, *membrana*, skin) is a thin barrier that permits selective mass transport. Between 1850 and 1900, membranes were used to derive basic physical principles for gas and liquid transport across a barrier material (see the work of Mitchell, Fick and Graham). In these early studies it was already recognized that membranes could be used to separate fluid mixtures. Membranes used at that time included dense films of nitrocellulose, natural rubber, and palladium. The first commercial synthetic membranes were developed by Bachmann and Zsigmondy in the early 1920s in Germany. These microporous nitrocellulose membranes were used for laboratory purposes as well as for the fast detection of bacteria in drinking water. However, until the early 1960s, membranes were not used in any industrial separation process. The major event that ultimately resulted in the widespread use of membranes for separations was the development of integrally-skinned, asymmetric cellulose acetate membranes for water desalination, by Loeb and Sourirajan at UCLA from 1958 to 1960. During a time span of only 10 years, a wide variety of membranes was developed for reverse osmosis, ultrafiltration and microfiltration applications based on modifications of the original membrane preparation method employed by Loeb and Sourirajan. Further-

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Table 1 Major milestones in the development of membranes for industrial separations

Period of years	*Advances*
1900–1920	Development of first ultrafiltration and microfiltration membranes made from nitrocellulose (Bechhold, Zsigmondy, Bachmann).
1920–1940	Empirical studies on formation of phase inversion membranes (Bjerrum, Manegold, Elford). Development of cellulose acetate ultrafiltration membranes (Dobry, Duclaux).
1940–1960	Development of integrally-skinned asymmetric cellulose acetate membranes for water desalination by reverse osmosis (Loeb and Sourirajan).
1960–1970	Commercialization of reverse osmosis, ultrafiltration, microfiltration, and dialysis membranes.
1970–1980	Development of thin-film composite membranes made by interfacial polymerization (Cadotte, Riley). Cellulose acetate gas separation membranes (Schell).
1980–1990	Commercialization of gas separation and pervaporation membranes (Henis and Tripodi, Tusel, Brüschke).
1990–2000	Development of inorganic membranes for gas separation and pervaporation.
The next millennium	Commercialization of inorganic membranes.

more, methods of efficiently packaging membranes into modules (plate-and-frame, spiral-wound, and hollow-fibre) were developed during this period. Around 1980, the use of membranes for separations was established as a unit operation process in the chemical process industry. Further optimization of membrane preparation and modification methods from 1980 to 1990 made membrane separations competitive in gas separation and liquid separation applications. The most important production methods that resulted in the commercial use of synthetic membranes are listed in **Table 1**. Recent attention has been directed towards the development of inorganic membranes. Optimized inorganic membranes can have significantly better separation properties compared to state-of-the-art polymeric membranes. However, currently the main limitations for large-scale commercialization of inorganic membranes are their poor mechanical strength (brittleness) and extremely high manufacturing costs.

Membrane Types

Membranes can be distinguished based on their (i) geometry, (ii) bulk structure, (iii) production method, (iv) separation regime, and (v) application, as shown in **Figure 1**. Most commonly, membranes are produced in flat-sheet or tubular (hollow-fibre) geometry. Flat-sheet membranes are either packaged in plate-and-frame or spiral-wound modules, whereas tubular membranes are packaged in hollow-fibre modules. The choice of the optimum membrane and module type depends on a wide variety of process specific conditions. Although hollow-fibre modules offer the highest membrane area per module volume ratio, plate-and-frame and spiral-wound modules are also commonly used for large-scale separations because of their better control of fluid dynamics.

Membranes either have a symmetric (isotropic) or an asymmetric (anisotropic) structure. The structure of a symmetric membrane is uniform throughout its entire thickness, whereas asymmetric membranes have a gradient in structure. The flux of a fluid through a symmetric membrane is typically relatively low, as the entire membrane thickness contributes a resistance to mass transport. Asymmetric membranes consist of two structural elements, that is, a thin, selective layer and a microporous substructure. Typically, the bulk structure (99+%) of an asymmetric membrane is highly porous and provides only mechanical strength. Separation of a fluid mixture in an asymmetric membrane is performed in a very thin surface layer, which is typically of the order of 0.1–0.5 μm thick. The most common symmetric and asymmetric membrane types are shown in **Figure 2**.

Ideal Membranes for Separations

Membranes can be fabricated from a wide variety of organic (e.g. polymers, liquids) or inorganic (e.g. carbons, zeolites, etc.) materials. Currently, most commercial membranes are made from polymers. The properties of a membrane are controlled by the membrane material and the membrane structure. To be useful in an industrial separation process, a

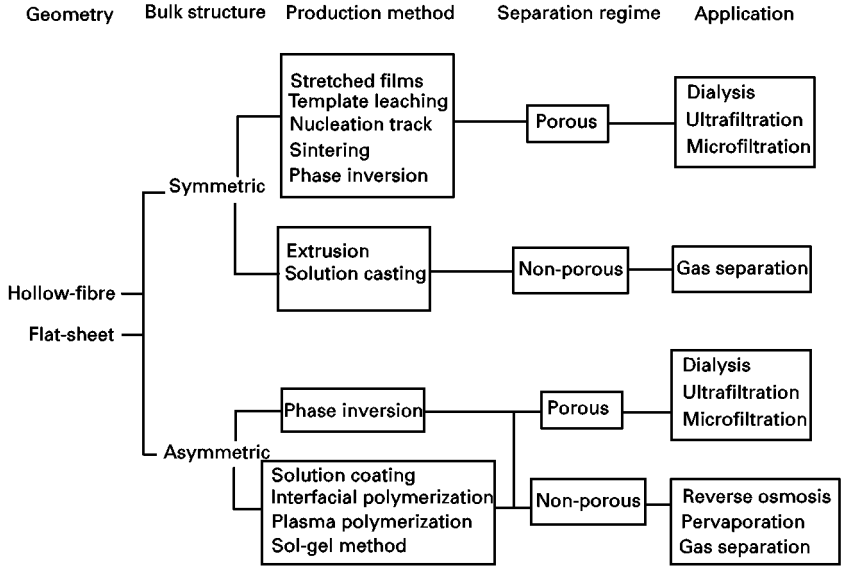

Figure 1 Classification scheme of synthetic membranes based on their geometry, bulk structure, production method, separation regime, and application.

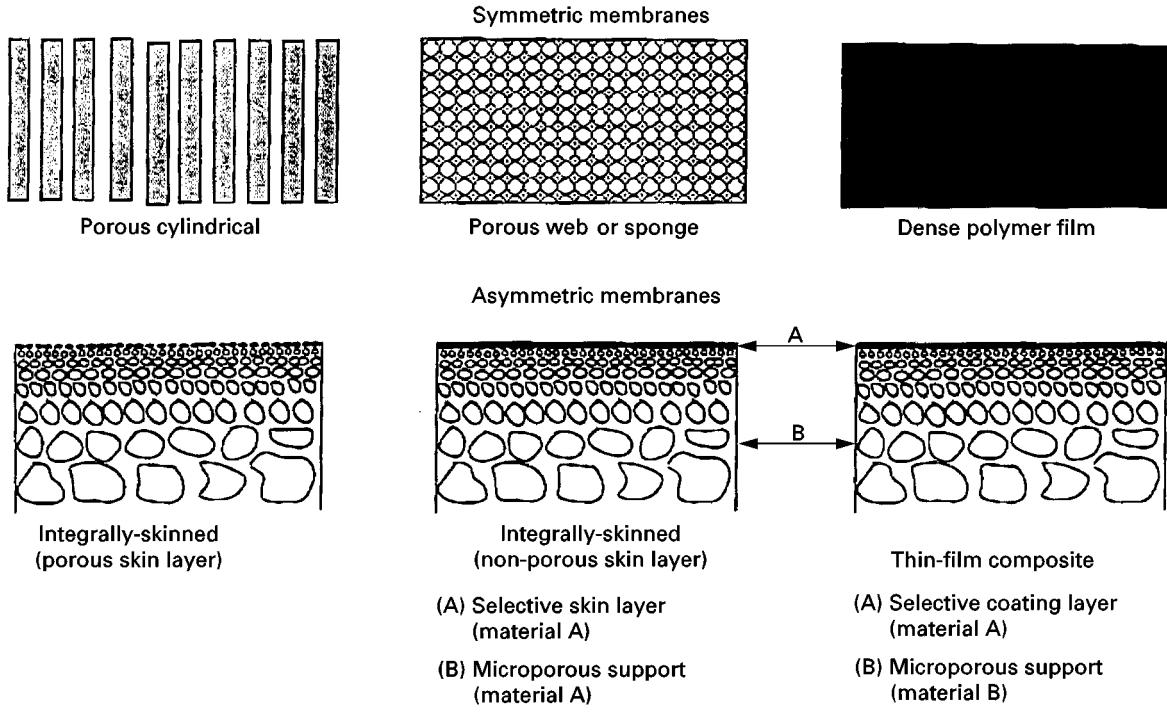

Figure 2 Schematic representation of symmetric and asymmetric membrane structures.

membrane must exhibit at least the following characteristics: (i) high flux, (ii) high selectivity (rejection), (iii) mechanical stability, (iv) tolerance to all feed stream components (fouling resistance), (v) tolerance to temperature variations, (vi) manufacturing reproducibility, (vii) low manufacturing cost, and (viii) ability to be packaged into high surface area modules. Of the above requirements, flux and selectivity (rejection) determine the selective mass transport properties of a membrane. The higher the flux of a membrane at a given driving force, the lower is the membrane area required for a given feed flow rate, and, therefore, the lower are the capital costs of a membrane system. The selectivity determines the extent of separation, and, therefore, the purity of the desired product.

Typically, porous membranes are used in dialysis, ultrafiltration, and microfiltration applications. Ideal porous membranes have high porosity and a narrow pore size distribution. Membranes having a dense, selective layer are applied in reverse osmosis, pervaporation, and gas separation processes. Permeation through dense membranes occurs by a solution/diffusion mechanism. Ideal dense membranes should have a very thin selective layer, because flux is inversely proportional to the membrane thickness. In addition, the thin separating layer must be pinhole-free, because even a very small area fraction of defects in the membrane can cause a significant decrease in selectivity.

Polymeric Membranes

Currently, most commercial membranes are made from polymers. Polymeric membranes can be fabricated by a wide variety of methods and fulfill most of the requirements of an ideal membrane listed above. Membranes are made from amorphous as well as semi-crystalline polymers by solution- or melt-processes. A list of commonly used polymers for commerical membrane separation processes is given in Table 2.

Symmetric Membranes

Dense Symmetric Membranes

Dense symmetric membranes with thicknesses greater than 10 μm can be made by melt extrusion or solution casting and subsequent solvent evaporation. Because the fluxes of fluids through dense polymer films are very low, this membrane type is rarely used for large-scale separations. Dense symmetric, ion-exchange membranes are used in electrodialysis applications for production of potable water from brackish water.

Porous Symmetric Membranes

Typically, symmetric porous membranes have cylindrical, sponge-, web- or slit-like structures, and can be made by a variety of techniques. The most

Table 2 Polymers used for production of commercial membranes

Membrane material	
Cellulose regenerated	D, UF, MF
Cellulose nitrate	MF
Cellulose acetate	GS, RO, D, UF, MF
Polyamide	RO, NF, D, UF, MF
Polysulfone	G, UF, MF
Poly(ether sulfone)	UF, MF
Polycarbonate	GS, D, UF, MF
Poly(ether imide)	UF, MF
Poly(2,6-dimethyl-1,4-phenylene oxide)	GS
Polyimide	GS
Poly(vinylidene fluoride)	UF, MF
Polytetrafluoroethylene	MF
Polypropylene	MF
Polyacrylonitrile	D, UF, MF
Poly(methyl methacrylate)	D, UF
Poly(vinyl alcohol)	PV
Polydimethylsiloxane	PV, GS

MF = microfiltration; UF = ultrafiltration; NF = nanofiltration; D = dialysis; PV = pervaporation; GS = gas separation.

important methods for the production of symmetric porous membranes are: (i) irradiation, (ii) stretching of a melt-processed semi-crystalline polymer film, (iii) template leaching, (iv) temperature-induced phase separation, and (v) vapour-induced phase separation.

Symmetric membranes with a cylindrical pore structure can be produced by an irradiation-etching process. These membranes are often referred to as nucleation track membranes. In the first step of this process, a dense polymer film, such as polycarbonate or polyester, is irradiated with charged particles, which cause chain scission and leave behind a sensitized track of damaged polymer molecules. These tracks are more susceptible to attack by chemical agents than the undamaged, base polymer film. In the second step, the film is passed through an etching medium, typically a sodium hydroxide solution. During this process, pores are formed by etching the partially degraded polymer along the nucleation tracks. Membranes made by this method have a very uniform pore size. The porosity and pore size of nucleation track membranes can be controlled by the irradiation time and etching time, respectively.

Membranes with a symmetric slit-like pore structure can be made from semi-crystalline polymers, such as polyethylene, polypropylene or polytetrafluoroethylene, using a melt extrusion/stretching process. In the first process step, a highly oriented film is formed by melt-extrusion of a semi-crystalline polymer and re-crystallization under high stress. The crystallites in the semi-crystalline polymer film are then aligned in the direction of orientation. In the second step, slit-like pores, about 200–2500 Å wide, are formed between the stacked lamellae by stretching the membrane in the machine direction. The pore size of these membranes is determined by the rate and extent of stretching during the second process step. Commercial membranes made by the extrusion/stretching process are available from Hoechst–Celanese (Celgard®) and W.L. Gore (Gore-Tex®).

Template leaching is another method of producing symmetric microporous membranes by melt-processing of a semi-crystalline polymer. In this process, a leachable component, such as a high-boiling paraffin, is uniformly dispersed in a polymer melt. After extrusion and formation of a polymer film, the leachable component is extracted using a suitable solvent, and a sponge-like, microporous membrane is formed.

Symmetric porous membranes can also be made by a thermally-induced phase separation process (TIPS process). In the TIPS process, the membrane structure is formed by bringing an initially thermodynamically stable polymer solution to an unstable state by lowering the process temperature. The change in temperature causes phase separation of the initially stable solution into two phases with different compositions. The membrane structure depends primarily on the initial polymer concentration and the kinetics of the phase separation process and the local distribution of the polymer-rich phase at the point of solidification. A schematic phase diagram for a solution containing a polymer and a solvent is shown in **Figure 3**. The phase diagram is divided into three distinct regions: (A) stable polymer solution region, (B) metastable or binodal region, and (C) spinodal region. Phase separation can occur by two different mechanisms, that is, (i) nucleation and growth or (ii) spinodal decomposition. The quench paths of three different polymer-solvent solutions from temperature T_1 to temperature T_2 are illustrated in Figure 3. After lowering the initial solution temperature T_1 to T_2, solutions A and B will be in the meta-stable region of the phase envelope and phase separation will occur by nucleation and growth. Solution A forms nuclei with composition ϕ_p^β (polymer-rich), whereas solution B will form nuclei with composition ϕ_p^α (solvent-rich). At equilibrium, both solutions phase-separate into two phases composed of ϕ_p^α and ϕ_p^β. However, the ratio of α-phase to β-phase is significantly different after phase separation of both solutions. Solution A will consist of a very small volume fraction of polymer-rich-phase (ϕ_p^β) dispersed in a large volume fraction of solvent-rich phase (ϕ_p^α). As a result of the low volume fraction of polymer, solution A will form a fine powder of precipitated polymer. On the other hand, solution B will consist of a small volume

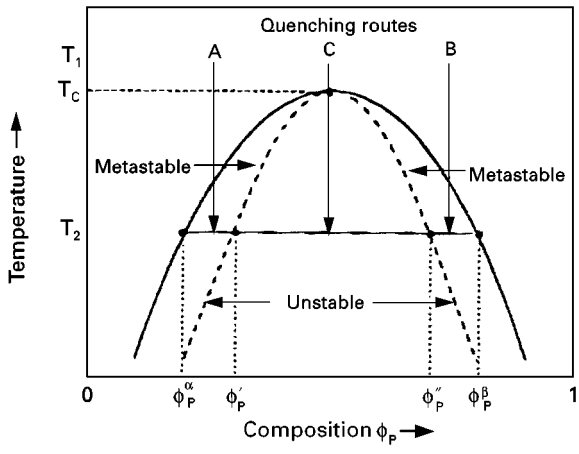

Figure 3 Schematic diagram of a binary polymer-solvent system with an upper critical solution temperature (UCST).

fraction of solvent-rich phase dispersed in a large volume fraction of polymer-rich phase. The resulting morphology is a sponge- or foam-like porous structure. A thermal quench of solution C passes directly into the unstable region of the phase diagram; therefore, phase separation occurs by spinodal decomposition. Typically, phase separation by spinodal decomposition leads to an interconnected, porous structure. The final membrane structure depends not only on liquid–liquid phase separation phenomena but also on the kinetics of the thermal quench process and the distribution of the polymer-rich phase at the point of solidification. Typically, a rapid quench rate results in a large fraction of small pores, whereas a slow quench rate produces fewer, but larger pores.

Symmetric membranes with sponge- or web-like pore structures can also be made by a vapour-precipitation/evaporation technique. Membranes made by this method are highly porous and are typically used in microfiltration applications. In its simplest form of the method, a solution containing polymer, solvents and non-solvents is cast onto a substrate and is then exposed to a water-vapour-saturated air stream. The water vapour induces phase separation in the initially stable polymer solution. After phase separation, the solvent and non-solvent components are evaporated by blowing a hot air stream across the membrane. The porosity and pore size of this membrane type can be controlled by: (i) the polymer concentration in the casting solution and (ii) the composition of the vapour atmosphere. Low polymer concentration, high humidity, and the addition of solvent-vapour to the casting atmosphere lead to membranes with high porosity and large pore size. Because membranes made by the vapour-precipitation/evaporation method have an essentially constant polymer concentration profile throughout the entire membrane thickness at the onset of phase separation, the resulting membranes are porous and have a fairly symmetric structure.

Asymmetric Membranes

The most commonly used asymmetric membranes are: (i) integral-asymmetric with a porous skin layer, (ii) integral-asymmetric with a dense skin layer, and (iii) thin-film composite membranes. Integrally-skinned asymmetric membranes are typically made by a non-solvent induced phase separation process (immersion precipitation) and consist of a thin, selective layer and a porous substructure. Both skin layer and substructure are formed simultaneously during the immersion precipitation process. Porous integral-asymmetric membranes are applied in dialysis, ultrafiltration, and microfiltration applications, whereas integral-asymmetric membranes with a dense skin layer are used in reverse osmosis and gas separation applications. Thin-film composite membranes consist of a thin, selective polymer layer atop a porous support. In this membrane type, the separation and mechanical functions are assigned to different layers in the membrane. This membrane type was originally developed for reverse osmosis applications; however, nowadays thin-film composite membranes are also used in nanofiltration, gas separation, and pervaporation applications.

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Integrally-Skinned Asymmetric Membranes

The first integrally-skinned asymmetric membranes were developed by Loeb and Sourirajan in the early 1960s for seawater desalination by reverse osmosis. In the original Loeb–Sourirajan technique, thin-skinned ($\sim 0.2\ \mu m$) cellulose acetate membranes were made by a four-step process: (i) casting of a multicomponent polymer solution, (ii) partial evaporation of a volatile solvent, (iii) immersion of the nascent polymer film into a non-solvent (water), and (iv) thermal annealing of the water-wet membrane. Membranes made by this method had water fluxes orders of magnitude higher than those of thick, isotropic cellulose acetate films while maintaining high sodium chloride rejection ($> 90\%$). The Loeb–Sourirajan method has been modified and applied to a wide variety of polymers other than cellulose acetate. In fact, the Loeb–Sourirajan process is by far the most important method for production of commercial membranes for separations.

In the simplest case, integrally-skinned asymmetric membranes are made from a binary solution containing a polymer and a solvent. Upon immersion of the cast solution into a liquid (typically water), which is

a non-solvent for the polymer but miscible with the solvent, an asymmetric structure with either a porous or non-porous skin layer is formed. The structural gradient in an integrally-skinned asymmetric membrane results from a very steep polymer concentration gradient in the nascent membrane at the onset of phase separation. The structure of a typical membrane made by immersion precipitation having a highly porous substructure and a thin skin layer is shown in **Figure 4**(A) and 4(B). In the immersion precipitation process, phase separation can be induced by: (i) solvent evaporation and/or (ii) solvent/non-solvent exchange during the quench step. Typically, the formation of membranes made by the immersion precipitation method occurs over a very short time scale, typically less than a few seconds. Most commercial membranes made by the immersion precipitation method are made from multi-component solutions containing polymer, solvent(s), and non-solvent(s) or additives. The porosity, pore size, and skin layer thickness can be modified by the addition of non-solvents to the casting solution (e.g. alcohols, carboxylic acids, surfactants, etc.), inorganic salts (e.g. $LiNO_3$ or $ZnCl_2$, etc.) or polymers (e.g. polyvinylpyrrolidone, polyethylene glycol, etc.). Even very small amounts of these solution additives can have a significant effect on the membrane structure, and hence, its separation properties. The structure of membranes made by immersion precipitation can also be altered by using multi-component quench media. For example, the addition of a solvent to the quench medium results in an increase in the surface porosity and pore size of the membrane. The formation of membranes made by the immersion precipitation process depends on a large number of material- and process-specific parameters including:

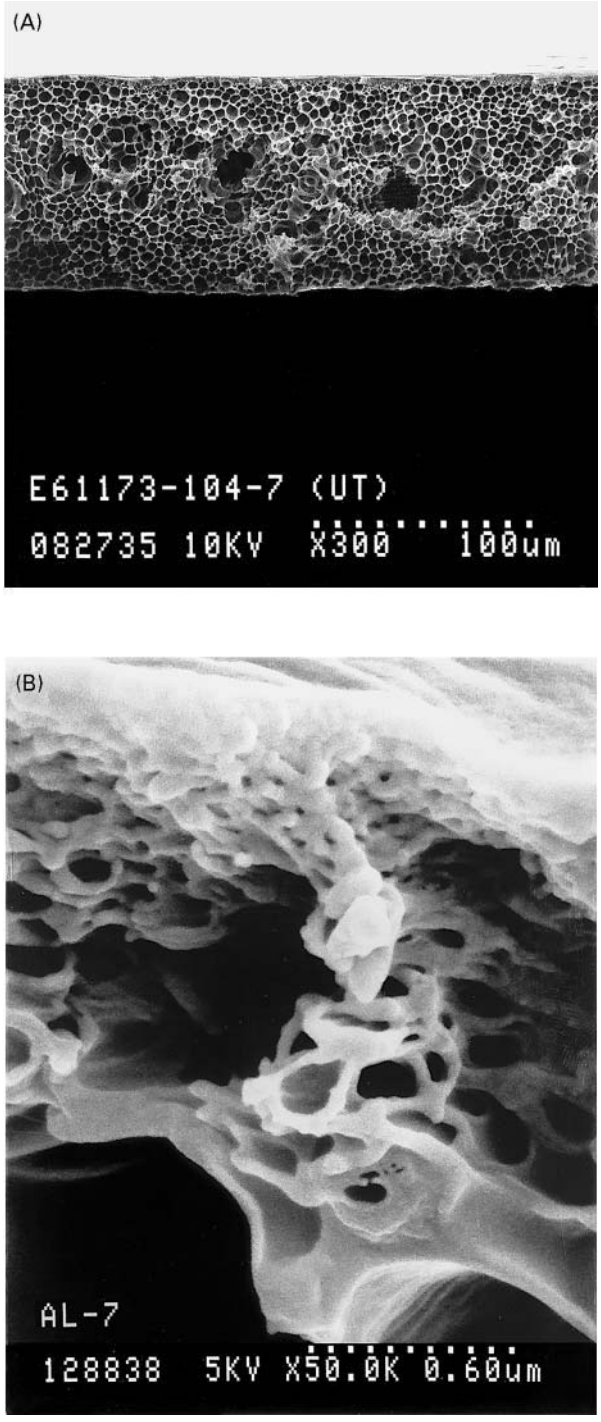

Figure 4 (A) Porous bulk structure and (B) skin layer of an integrally-skinned asymmetric polysulfone membrane made by the immersion precipitation process.

- choice of the polymer (molecular weight, molecular weight distribution)
- choice of the solvent(s) and additives
- composition of the casting solution
- choice of the quench medium
- composition and temperature of the casting atmosphere
- temperature of the casting solution and quench medium
- evaporation conditions
- casting thickness
- casting or spinning speed
- membrane support material (type of woven or non-woven)
- drying conditions.

Thin-Film Composite Membranes

Composite membranes consist of at least two structural elements made from different materials, as shown in **Figure 5**. A single-layer composite membrane (5A) consists of a thin, selective layer atop a microporous support. The support provides only mechanical strength, whereas the separation is

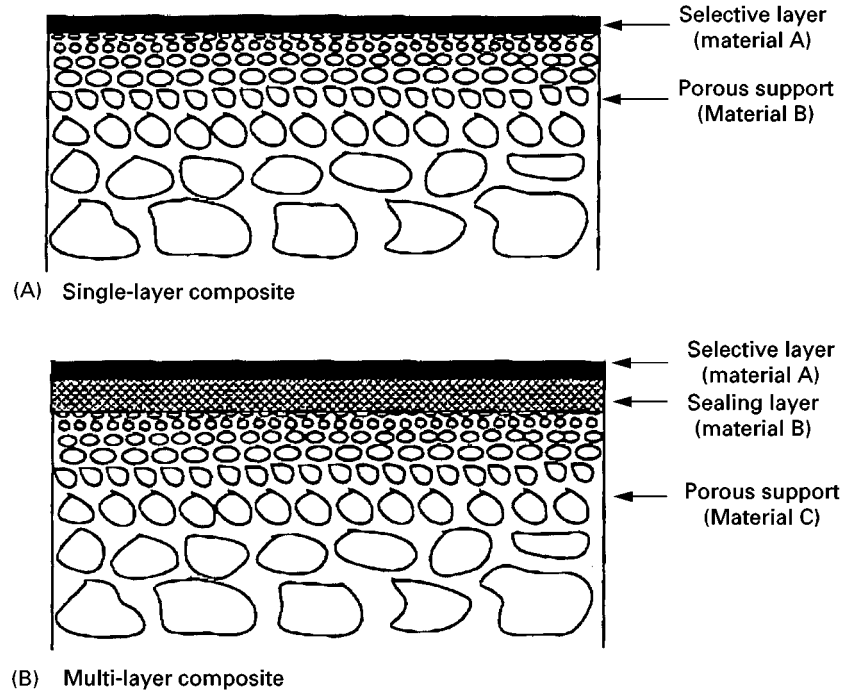

Figure 5 Schematic diagram of (A) single-layer and (B) multi-layer thin-film composite membranes.

performed by the thin top-layer. A multi-layer composite membrane (5B) consists of a porous support and several layers of different materials, each performing a specific function. Thin-film composite membranes are applied in nanofiltration, reverse osmosis, gas separation, and pervaporation applications. The selective layer can be applied by lamination, solution coating, interfacial polymerization, or plasma polymerization methods. Compared to integrally-skinned asymmetric membranes, composite membranes offer several significant advantages: (i) independent selection of materials from which the separating layer and the porous support are formed, (ii) independent preparation of the separating layer and the porous support membrane, thereby making it possible to optimize each structural element, and (iii) very expensive membrane materials (>1000 \$/lb) can be used because only a very small amount of polymer is required for the formation of the thin separation layer (~ 1 g polymer/m^2 of membrane for a 1-μm-thick selective layer).

In most cases, porous, ultrafiltration-type membranes made by the immersion precipitation process are used as mechanical support for thin-film composite membranes. Optimum porous supports for thin-film composite membranes should have the following properties: (i) porous support must be chemically resistant against the solvent or solvent mixture from which the thin separating layer is formed and (ii) the porous support should have a high surface porosity and small pore size. High surface porosity is important because the support should not provide any significant resistance to mass transport in a composite membrane. A small pore size is required for the deposition of ultrathin, defect-free coatings.

The two most important methods for the commercial production of thin-film composite are based on interfacial polymerization and solution coating methods. The first interfacially polymerized thin-film composite membranes were developed by Cadotte at the North Star Research Institute and represented a breakthrough in membrane performance for reverse osmosis applications. The original interfacial polymerization process involved soaking a microporous polysulfone support in an aqueous solution of a polymeric amine and then immersing the amine-impregnated membrane into a solution of a di-isocyanate in hexane. The membrane was then cross-linked by heat-treatment at 110°C. The resulting polyurea membrane had better salt rejection than that of an integrally-skinned asymmetric cellulose acetate membrane and high water flux. Modifications in the chemistry of the original interfacial polymerization reaction scheme resulted in further improvement in performance of thin-film composite membranes for reverse osmosis applications.

The solution-coating method involves deposition of a dilute polymer solution onto the surface of a porous membrane and subsequent drying of the thin liquid film. The simplicity of this process is very attractive for the production of membranes on a

commercial scale. However, it is generally very difficult to produce defect-free thin-film composite membranes with a thickness of less than 1 μm by the solution coating process. These defects are caused by incomplete coverage of surface pores in the support membrane after complete evaporation of the solvent. The difficulty in completely covering surface pores results from penetration of the coating solution into the porous support membrane structure. Because capillary forces in the porous membrane tend to pull the thin liquid polymer solution into the bulk support membrane, the coating layer can be disrupted easily. Several methods have been proposed to overcome problems with the formation of the thin, selective layer by the solution-coating process. One method is to use ultrahigh molecular weight polymers for the formation of the selective layer. An alternative approach for eliminating defects in the thin selective coating layer is to fabricate multi-layer composite membranes. These membranes, shown schematically in Figure 5B, consist of: (i) a porous support, (ii) a sealing layer, and (iii) an ultrathin, selective coating. The function of the sealing layer is to plug the pores in the support membrane and to provide a smooth surface onto which the thin coating layer can be applied. In addition, the sealing layer helps in channeling the permeating components to the surface pores, thereby rendering the entire surface area available for mass transport. The sealing layer should not provide a significant mass transport resistance in a multi-layer composite membrane. Hence, the sealing layer material should be significantly more permeable than the thin, selective top-layer.

Membrane Modification Methods

The development of high-performance polymeric membranes involves the selection of a suitable membrane material and the formation of this material into a desired membrane structure. However, it is often necessary to modify the membrane material or the structure to enhance the overall performance of the membrane. Generally, the objectives for modification of pre-formed membranes are: (i) increasing flux and/or selectivity and (ii) increasing chemical resistance (solvent resistance, swelling, or fouling resistance).

The first reported membrane modification method involved annealing of porous membranes by heat-treatment. Zsigmondy and Bachmann demonstrated in the early 1920s that the pore size of pre-formed nitrocellulose membranes could be decreased with a hot water or steam treatment. Loeb and Sourirajan used the same method to improve the salt rejection of integrally-skinned asymmetric cellulose acetate reverse osmosis membranes.

During the development of integrally-skinned asymmetric cellulose acetate gas separation membranes it was found that water-wet membranes collapse and form an essentially dense film upon drying. This collapse occurs because of the strong capillary forces within the finely porous structure during the drying process. This phenomenon can be described by the well-known Young–Laplace relationship ($(\Delta p = 2\gamma/r)$ in the case of perfect wetting of the liquid in the pores). Hence, the capillary pressure is directly proportional to the surface tension of a liquid, but inversely proportional to the pore radius. If the modulus of the membrane material (in the swollen state) is lower than the capillary force of the liquid in the pore space, the pores will collapse and form a dense polymer film. Because water has a very high surface tension, it is often difficult to dry water-wet membranes without collapsing the membrane structure. An exchange of water with liquids having lower surface tension, such as alcohols or aliphatic hydrocarbons, results in maintaining the original membrane structure upon drying. Typical solvent-exchange methods involve replacing water first with *iso*-propanol and then with *n*-hexane. Other methods of eliminating the collapse of finely porous membrane structures include freeze-drying and the addition of surfactants to the water prior to drying of the wet membranes.

In the 1970s, commercialization of gas separation membranes was severely limited by the very poor reproducibility of making ultrathin, defect-free membranes on a large scale. Methods for production of thin-film composite membranes as well as integrally-skinned asymmetric membranes with separating layer thicknesses of less than 0.2 μm were known. However, production of these membranes without defects was not possible. Defects as small as 20 Å over an area fraction of less than 10^{-4}% can severely reduce the selectivity of gas separation membranes. However, a thin coating of a highly permeable polymer, such as polydimethylsiloxane, can render defective membranes suitable for gas separations. Modification methods developed by Browall for thin-film composite membranes and, in particular, Henis and Tripodi for integrally-skinned asymmetric membranes resulted in rapid commercialization of gas separation membranes. Surface coatings are also applicable in improving the fouling resistance of membranes for ultrafiltration or nanofiltration applications. Chemical surface modification methods of gas separation membranes include treatment with fluorine, chlorine, bromine, or ozone. Typically, these treatments result in an increase in membrane selectivity coupled with a decrease in flux. Cross-linking of polymers is often applied to improve the chemical stability (swelling

resistance) and selectivity of membranes for electrodialysis, reverse osmosis, pervaporation, and gas separation applications.

Inorganic Membranes

Ceramic Membranes

Microporous ceramic membranes for ultrafiltration and microfiltration applications can be formed from a variety of metal oxides. Specifically, aluminium and titanium oxides are preferred precursors for the production of ceramic membranes. Because ceramic membranes are chemically inert and can be operated at high temperatures, these membranes offer some significant advantages over polymeric membranes. Pore diameters in ceramic membranes for ultrafiltration and microfiltration are in the 0.01 to 10 μm range and are typically made by a slip coating-sintering process. Other techniques, such as the sol-gel method, produce ceramic membranes with pores in the range of 10 to 100 Å. In the slip coating-sintering process, a porous ceramic tube is made by pouring a dispersion of a coarse ceramic material and a binder into a mould. This mixture is then sintered at high temperature. The resulting porous tube is then coated with a mixture containing very small metal oxide particles and a binder; this mixture is called a slip suspension. Again, the mixture is sintered at high temperature to form a more finely porous layer. The slip-coating-sintering method can be used to make membranes with pore diameters between 100 to 200 Å. More finely porous membranes can be fabricated by the sol-gel technique. First, the metal oxide, dissolved in alcohol, is hydrolyzed by addition of excess water. Then, the colloidal polymeric or inorganic hydroxide solution is cooled and coated onto a preformed microporous support made by the slip coating-sintering process. The coating must be dried very carefully to avoid cracking of the thin ceramic layer. The final step of the sol-gel method involves sintering of the coating at elevated temperature, typically between 500 and 800°C. In principle, membranes made by this process can be used in a variety of applications which require membranes that are stable in harsh environment and at elevated temperature. However, reproducibility of the membrane formation process on a large commercial scale is rather poor and the membrane costs are too high for these membranes to be used in any industrial separation process.

Metal Membranes

Metal membranes have been considered for a long time for gas separation applications, specifically hydrogen separation. Certain noble metals, for example palladium or palladium–silver and palladium–gold alloys, are permeable to hydrogen but essentially impermeable to all other gases. In the 1950s and 1960s, Union Carbide installed a pilot membrane system containing 25-μm-thick, isotropic palladium membranes. Because the hydrogen flux through these thick palladium membranes is quite low, the membranes had to be operated at about 400°C. Although the plant generated 99.9% hydrogen, commercialization of this process was economically not feasible because of the extremely high cost of the metal membrane ($\sim$ \$5000/m^2). Furthermore, contaminants in the feed stream, such as hydrogen sulfide, poison the metal which results in a dramatic decline in hydrogen flux.

Anodic Membranes

Symmetric and asymmetric microporous membranes with a conical pore shape can be made from aluminium using an anodic oxidation process. Symmetric aluminium oxide membranes having a porosity of 65% and a pore size of about 200 nm can be made. The surface pores of asymmetric aluminium oxide membranes are about 25 nm. To prepare these membranes, a thin aluminium foil is anodically oxidized in an acid electrolyte, such as sulfuric or chromic acid, thereby forming an aluminium oxide. The unaffected fraction of the metal foil is subsequently removed using a strong acid. The pore size of membranes made by anodic oxidation is determined by the voltage and the acid type.

Carbon Membranes

Microporous carbon membranes can be made by compressing ultrafine carbon particles or by pyrolysing polymeric precursors. Degradation of the base polymer upon heating leads to carbonization. The pore size and porosity of the pyrolysed membranes depend primarily on the pyrolysis temperature and the pyrolysis atmosphere. Molecular sieve membranes made from pyrolysed polyacrylonitrile and polyimide as well as selective surface flow membranes made from polyvinylidene chloride-acrylate terpolymer can have significantly better separation performance than polymeric membranes in gas separation applications. The pore sizes of microporous carbon membranes are typically in the 5 to 20 Å range.

Glass Membranes

Isotropic glass membranes with a sponge structure can be made by thermal phase separation of an initially homogenous metal oxide mixture. Microporous

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glass membranes were produced by Corning (Vycor®), Schott, and PPG. Glass membranes are typically made as discs, tubes or hollow-fibres. To produce microporous glass membranes, a homogeneous melt consisting of 70 wt% SiO_2, 23 wt% B_2O_3 and 7 wt% Na_2O is formed between 1300 to 1500°C. Phase separation of the initially homogeneous glass melt occurs by lowering the temperature to about 800°C. One phase consists primarily of insoluble silicon dioxide. The other phase, rich in alkali borate, can be leached from the heterogeneous glass by treatment with a mineral acid. After removal of the alkali borate phase, a microporous silica membrane is formed.

Future Developments

During the past forty years membranes have gained significant importance in a wide variety of industrial separations. Currently, polymeric membranes are most commonly used for commercial applications. However, recent developments on inorganic membranes are very promising and such membranes may broaden the separation spectrum of membranes for separations. The wide-spread use of inorganic membranes in industrial applications is currently limited by their poor mechanical stability and very high production costs. If these problems can be solved in future work, inorganic membranes will present a new generation of high-performance membranes for the next millennium.

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Microfiltration

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Introduction

Microfiltration is a separation technique for removing micron-sized particles, like bacteria, yeast cells, colloids, and smoke particles, from suspensions or gases. The process uses membrane filters with pores in the approximate size range 0.1 to 10 μm, which are permeable to the fluid, but retain the particles, thus causing separation. Examples of particles with sizes in the microfiltration range are presented in **Figure 1**.

Microfiltration membranes were first commercialized in the 1920s, and were at that time mainly used for the bacteriological analysis of water. After 1960 the number of successful microfiltration applications grew rapidly, and nowadays microfiltration processes are operated in such different fields as the biotechnological, automobile, electronics, and food industry. Examples of applications are the harvesting of bacterial and yeast cells, the recovery of latex pigments from paints, and the purification of water for the electronics industry. In the food industry, microfiltration is used in the clarification of fruit juices, wine, and beer, in fat removal from whey and in removal of bacteria from milk.

Microfiltration is the largest industrial market within the membrane field, responsible for about 40% of total sales, both in Europe and in the USA. In 1997, the US microfiltration membrane market amassed revenues worth about $400 million, growing at an average annual growth rate of 6.6%. Microfiltration can be carried out in two different operation modes: dead-end (in line) filtration and cross-flow